

**THERMALLY STIMULATED CATIONIC  
POLYMERIZATION OF 2-ETHYL-2-OXAZOLINE  
BY CATIONIC SALTS**

**M. Sc. Thesis by**

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**Department : Polymer Science and Technology**

**Programme: Polymer Science and Technology**

**JANUARY 2004**

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**JANUARY 2004**

**İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**

**2-ETİL-2-OKZAZOLİNİN KATYONİK  
TUZLARLA İSİSAL KATYONİK  
POLİMERİZASYONU**

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December 2003

Halil KİRLİBAL

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## LIST of ABBREVIATIONS

<b>EOZO</b>	: 2-Ethyl-2-oxazoline
<b>BPYBr</b>	: <i>N</i> -Benzyl Pyridinium Bromide
<b>B-<i>o</i>-CNPyBr</b>	: <i>N</i> -Benzyl 2-Cyano Pyridinium Bromide
<b>B-<i>p</i>-CNPyBr</b>	: <i>N</i> -Benzyl 4-Cyano Pyridinium Bromide
<b>BDMABr</b>	: <i>N</i> -Benzyl- <i>N,N</i> -Dimethylanilinium Bromide
<b>BTPhPBr</b>	: <i>N</i> -Benzyl Triphenyl Phosphonium Bromide
<b>PDMABr</b>	: <i>N</i> -Phenacyl- <i>N,N</i> -Dimethylanilinium Bromide
<b>On<sup>+</sup></b>	: Onium Salt
<b>DIP</b>	: Double Isomerization Polymerization
<b>MeOTs</b>	: <i>p</i> -Toluenesulfonate
<b>MeOTf</b>	: Methyl Trifluoromethanesulfonate
<b>TMS</b>	: Tetramethylsilane
<b>EMP<sup>+</sup>PF<sub>6</sub><sup>-</sup></b>	: <i>N</i> -Ethoxy-2-Methylpyridinium Hexafluorophosphate
<b>EPP<sup>+</sup></b>	: <i>N</i> -Ethoxy-4-cyanopyridinium
<b>EIQ<sup>+</sup></b>	: <i>N</i> -ethoxyisoquinolinium
<b>Ph</b>	: Phenyl Group
<b>Py</b>	: Pyridine Group
<b>R</b>	: Alkyl Group
<b>NMR</b>	: Nuclear Magnetic Resonance Spectroscopy
<b>GPC</b>	: Gel Permeation Chromatography
<b>IR</b>	: Infrared Spectrophotometer
<b>UV</b>	: Ultra Violet
<b>M<sub>n</sub></b>	: Number Average Molecular Weight

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## **THERMALLY STIMULATED CATIONIC POLYMERIZATION OF 2-ETHYL-2-OXAZOLINE BY CATIONIC SALT**

### **SUMMARY**

In this thesis, thermally stimulated cationic polymerization of cyclic iminoethers, namely 2-ethyl-2-oxazoline (EOZO), was investigated. 2-Oxazolines are five-membered cyclic imino ethers, which are heterocyclic compounds with an imino ether linkage. Cationic ring-opening polymerization of cyclic imino ethers generally involves a thermodynamically favourable isomerization of the imino ether groups to the amide. Oxazoline monomers give thermal cationic polymerizations with benzyl bromide. The aim of this study was to obtain benzylic cation with bromide counter anion, which serves as a cationic initiator in thermal or photochemical polymerizations. In this sense, salts containing a series of photochemically and thermally active hetero atoms were synthesized and their activities in polymerization were investigated. The salts with bromide counter anions were usually formed as an intermediate and directly converted to non-nucleophilic ones without isolation. Therefore, synthesis and characterization of the isolated salts with bromide anions were reported for the first time in this work.

## **2-ETİL-2-OKZAZOLİNİN KATYONİK TUZLARLA İSİSAL KATYONİK POLİMERİZASYONU**

### **ÖZET**

Bu çalışmada halkalı imino eterlerden 2-etil-2-okzazolinin ısısal uyarılarak katyonik polimerleşmesi incelenmiştir. 2-Okzazolin monomerleri 5 halkalı imino eter grubundandır ve yapısında heterosiklik bileşikle birlikte imino eter bağı içerir. Halkalı imino eterlerin katyonik halka açılma polimerizasyonu, imino eterlerin amide ısısal olarak isomerizasyonu ile gerçekleşir. Okzazolin monomerlerinin ısısal olarak benzil bromür ile katyonik polimerizasyona uğradığı bilinmektedir. Çalışmamızda benzil bromürün dolaylı olarak katyonik tuzlardan ısısal ve fotokimyasal yollar kullanılarak oluşturulması ve polimerleşmeyi başlatması amaçlanmaktadır. Bu doğrultuda, fotokimyasal ve ısısal aktif bir seri hetero atom içeren tuzlar sentezlenmiş ve polimerizasyondaki aktiviteleri incelenmiştir. Brom karşı anyonuna sahip tuzlar genellikle ara ürün olarak bulunurlar ve izole edilmeden karşı iyonları düşük nükleofilli bir karşı iyonla değiştirilirler. Buna karşın brom karşı iyonlu izole tuzların sentezi ve karakterizasyonu ilk defa bu çalışmada yer almıştır.

## 1. INTRODUCTION

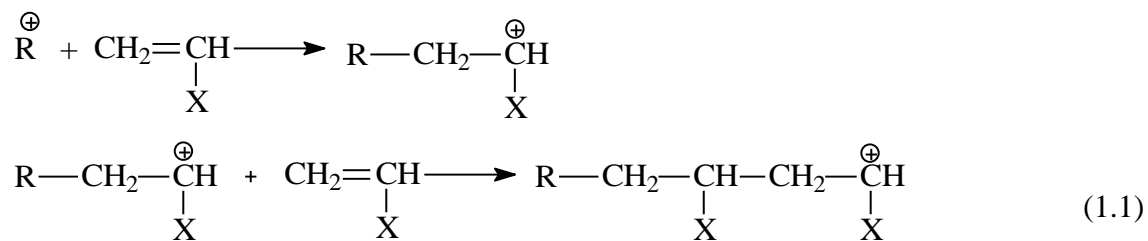
Initiators that generate reactive species capable of initiating cationic polymerizations by external stimulation-photolysis or heating-are extremely important in the control of the initiation step. The polymers obtained by using externally stimulated initiators usually show broad molecular weight distribution. The initiating species are continuously generated by thermolysis until all of the initiator is consumed. These external initiators overcome the problems of the classical initiators such as heterogeneous polymerization mixture, strong exothermic polymerization and requirement of low temperature polymerization. During the past two decades, considerable attention has been devoted to thermal or photo-latent system for the initiation of cationic polymerization [1]. Cationic polymerizations initiated this way are of great practical interest due to their applicability for the curing of coatings and printing inks, and for resist technology [2].

Cationic Polymerization of vinyl and cyclic monomers can be initiated by various initiators such as protonic and Lewis acids, carbocations, and trialkyl oxonium salts [3]. General reactions for the initiation of the polymerization may be presented as shown below (1.1, 1.2).

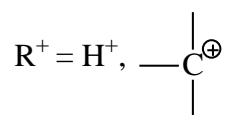
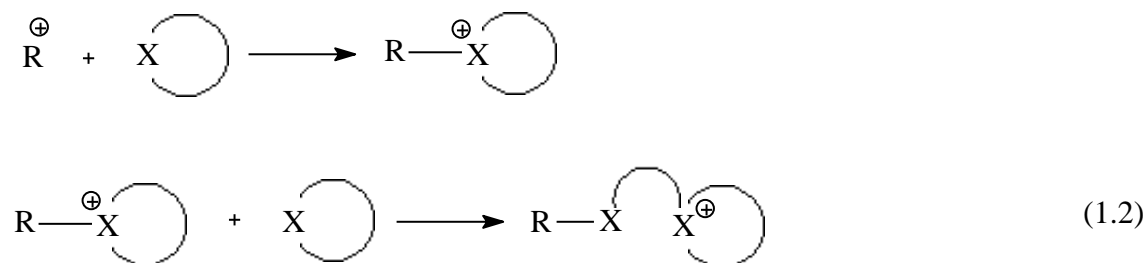
Some of the onium salts are activated thermolytically. However, mostly onium salts with slight differences in the pattern of substitution are used. For example, for photoinitiation N-alkoxy pyridinium salts serve as initiators whereas for thermal polymerization, N-benzyl pyridinium salts are utilized.

Besides the direct thermolysis of the initiator, also indirect methods have been reported. Thermally generated radicals can be used in radical oxidation and addition fragmentation schemes for producing appropriate initiating cations.

## Vinyl Monomers

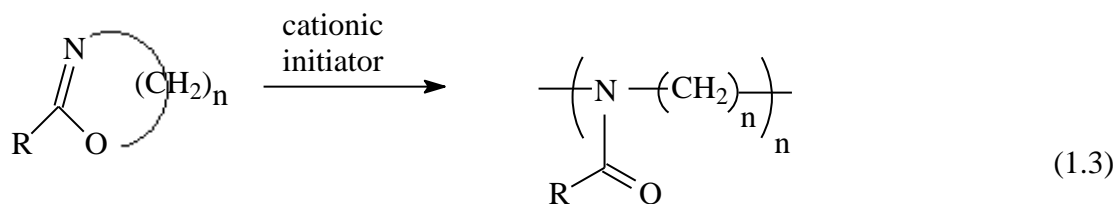


## Cyclic Monomers



Ionic polymerizations can be classified in three categories depending on the reactivity characteristics of the growing species, i.e., polymerizations via electrophilic, via nucleophilic, via zwitterionic propagating species. A typical example of polymerization via electrophilic growing species is seen in the ring-opening polymerization of 2-oxazolines.

2-Oxazolines are five-membered cyclic imino ethers, which are heterocyclic compounds with an imino ether linkage. Cationic ring-opening polymerization of cyclic imino ethers generally involves a thermodynamically favourable isomerization of the imino ether groups to the amide.



n= 2, 2-oxazolines

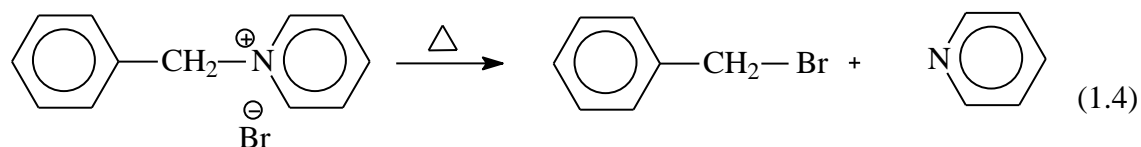
n=3,5,6-dihydro-4H-1,3-oxazines

Ring-opening isomerization polymerization of 2-oxazolines has aroused a great deal of interest in both polymerization chemistry and in the materials design of functional polymers. Numerous studies on 2-oxazoline polymer have been undertaken over the last thirty years.

Many different cationic initiators, such as Lewis acids, stable cationic salts, strong protonic acids and their salts, ester of sulfuric sulfonic and picric acids and acid anhydrides, and alkyl halides, have been employed for the polymerization of 2-oxazolines.

Cationic polymerization of 2-oxazolines proceeds under anhydrous conditions. However, high vacuum experiments are not necessary. Reaction using carefully dried reagents and under nitrogen atmosphere is sufficient to prepare polymers having relatively narrow molecular weight distributions.

Oxazoline monomers give thermal cationic polymerizations with benzyl bromide. The aim of this study was to obtain benzylic cation with bromide counter anion, which serves as a cationic initiator in thermal or photochemical polymerizations.



In this sense, salts containing a series of photochemically and thermally active hetero atoms were synthesized and their activities in polymerization were investigated.

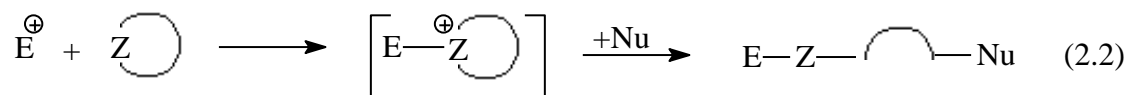
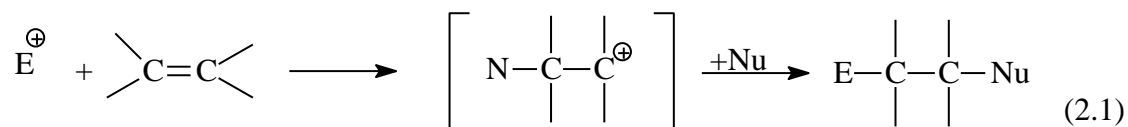
## **2. THEORETICAL PART**

### **2.1 Cationic Polymerization**

Within the context of polyaddition, cationic polymerization refers to chain growth reactions promoted by active species possessing electrophilic character: carbenium, carbonium, oxonium, sulfonium, ammonium and phosphonium ions, but also molecular chain carriers, i.e., mostly esters, which are sufficiently polarized to induce propagation. In these systems, the intrinsic structure and reactivity of the active species are maintained throughout the growth of a polymer molecule. Typical examples of such polyadditions are the cationic polymerizations of alkenyl monomers through the opening of the C=C double bond and of saturated heterocyclic monomers through ring-opening. The two systems differ in that the active species in the polymerization of alkenes are carbenium ions, whereas onium ions are the active species in the polymerization of heterocycles [4].

#### **2.1.1. Electrophilic Addition Mechanism and Monomers**

All polyadditions can be viewed as special cases of specific physical organic reactions in which the intermediate species manages to survive long enough to ensure the growth of a macromolecule instead of rapidly collapsing into inactive products. A cationic polymerization is a special case of electrophilic addition. Classical electrophilic additions to the two types of common monomers in cationic polymerization, i.e., to the olefinic bond in alkenyl compounds and to the heteroatom in saturated heterocyclic compounds, can be represented as where  $Z = O, S, N\text{---}, P\text{---}$  etc.



In cationic polymerization, the intermediates (2.1) and (2.2), shown as positively charged species must be prevented from collapsing through the reaction with an anion for long enough to allow them a large number of successive monomer additions.

#### 2.1.1.1. Cationic Polymerization of Vinyl Monomers

The monomers fitted for cationic polymerization include all those with electron donating substituents, in which the polarization of the double bond makes them sensitive to electrophilic attack by carbenium site.

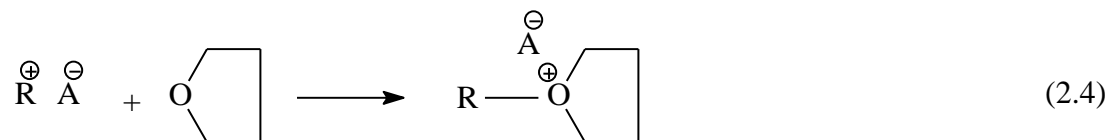


Solvents used in cationic polymerization should be stable towards acids and unable to react with electrophiles. Preferred are halogenated solvents such as methylene chloride, methyl chloride, ethylene chloride, and carbon tetrachloride, nitro compounds such as nitromethane or nitrobenzene and also dioxane.

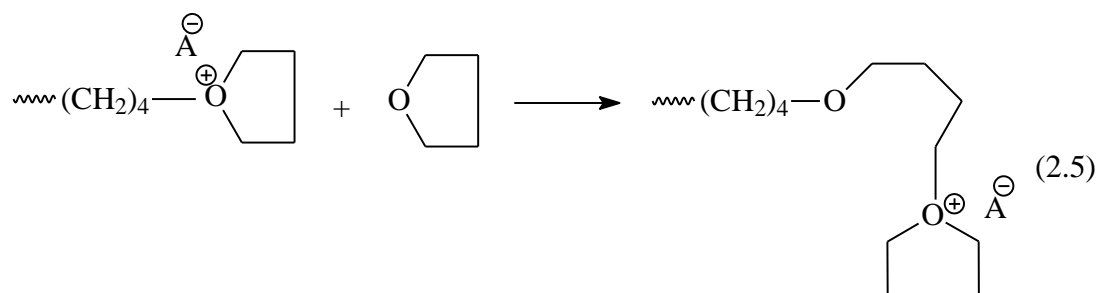
#### 2.1.1.2. Cationic Polymerization of Heterocycles

The ring opening polymerization of several heterocycles proceeds by cationic initiation via oxonium sites that are formed upon alkylation (or protonation) of the monomer:





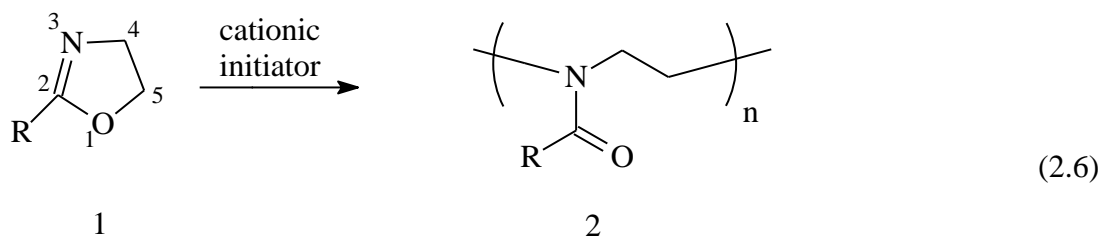
The mechanism of chain growth involves nucleophilic attack of the oxygen of an incoming monomer onto carbon atom in  $\alpha$ -position with respect to the oxonium site, whereby the cycle opens and the active site is reformed on the attacking unit.



## 2.2 Polymerization of 2-Oxazolines

The ring-opening polymerization of 2-oxazolines was first reported by Kayiga et al. in 1966 [10]. Polymerization of 2-methyl- and 2-phenyl-2-oxazoline was examined in acetonitrile and in the bulk.

Except for the case of Double Isomerization Polymerization (DIP) of 2-amino-2-oxazolines, 2-oxazolines are polymerized to produce the corresponding derivatives of poly [(*N*-acylimino) ethylene] (2) via ring-opening isomerization. The term poly (*N*-acylethylenimine) is even more common. The polymerization reaction of 2-oxazolines is not disturbed by chain transfer and termination under appropriate conditions. The cationic propagation species of an oxazolinium salt is not fragile. Therefore, it is conveniently employed in the synthesis of block copolymers and end-reactive polymers. The living character for polymerization of 2-oxazolines is mentioned in the previous reviews [11], [12].

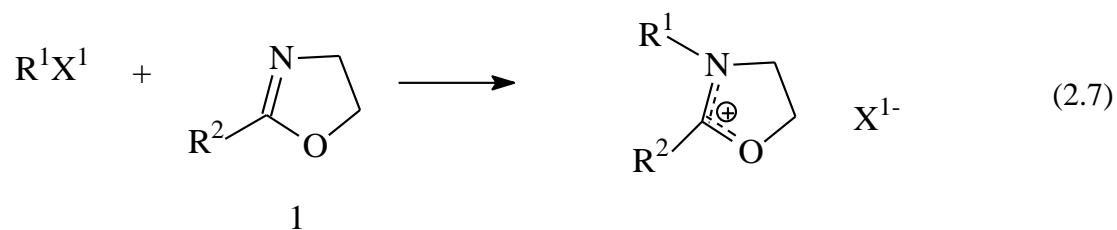


The ring-opening polymerization behavior of 2-oxazolines having a variety of 2-substituents has been extensively investigated by Seagusa, Kobayashi, and coworkers [5], [6], [7], [8]. General mechanism for initiation and propagation of 2-oxazolines are shown in Fig. 2.1. It has been interpreted that the reaction proceeds via two different types of species, i.e. ionic and covalent types, depending upon the nature of the initiator. In the cationic polymerization of 2-oxazolines 1, the nucleophilic attack of a nitrogen atom of 1 onto the C (5) carbon of the propagating 2-oxazolinium species 3 results in O (1)-C (5) bond cleavage and isomerization of 3 to give 4 having N-acylethylenimine units. On the other and, when  $R^3X^2$  is an initiator generating a weakly nucleophilic  $X^2$  anion, polymerization of 1 proceeds via covalent-bonded species (6 and 7). In this case, the ring of the generated 2-oxazolinium salt 5 is rapidly opened by the attack of the counter anion having higher nucleophilicity than of oxazoline monomer.

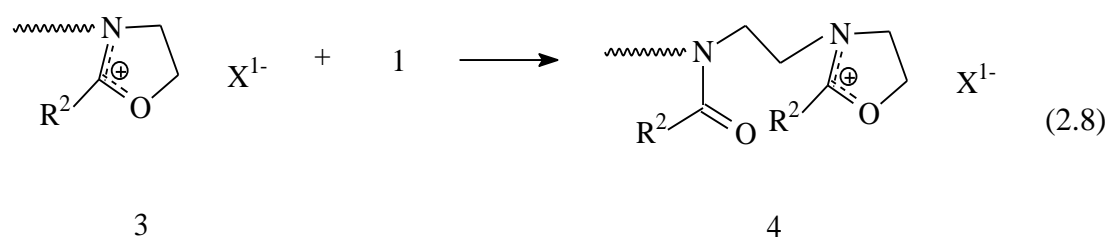
Recently, a novel covalent-type electrophilic polymerization for 2-oxazolines having perfluoroalkyl groups at the 2-position was revealed for the system using a sulfonate initiator [20], [12]. As illustrated in Fig. 2.2, with methyl *p*-nitrobenzenesulfonate or *p*-toluenesulfonate (MeOTs) initiators, the propagating species of the polymerization of 2-(perfluoroalkyl)-2-oxazolines involves a covalent sulfonate ester.

## Ionic Type

### Initiation

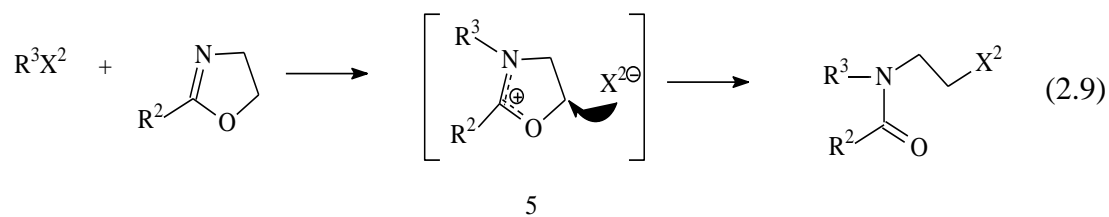


### Propagation



## Covalent Type

### Initiation



### Propagation

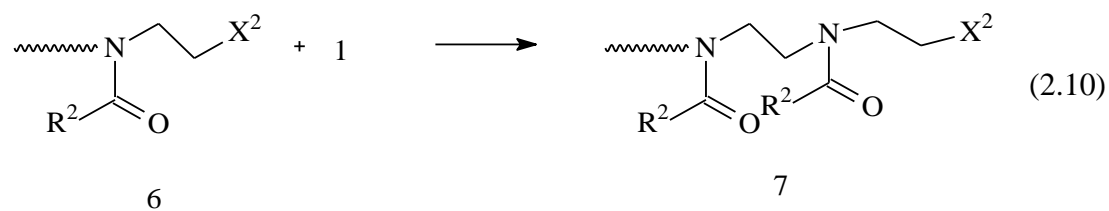


Figure 2.1. Types of polymerization mechanisms for 2-oxazolines

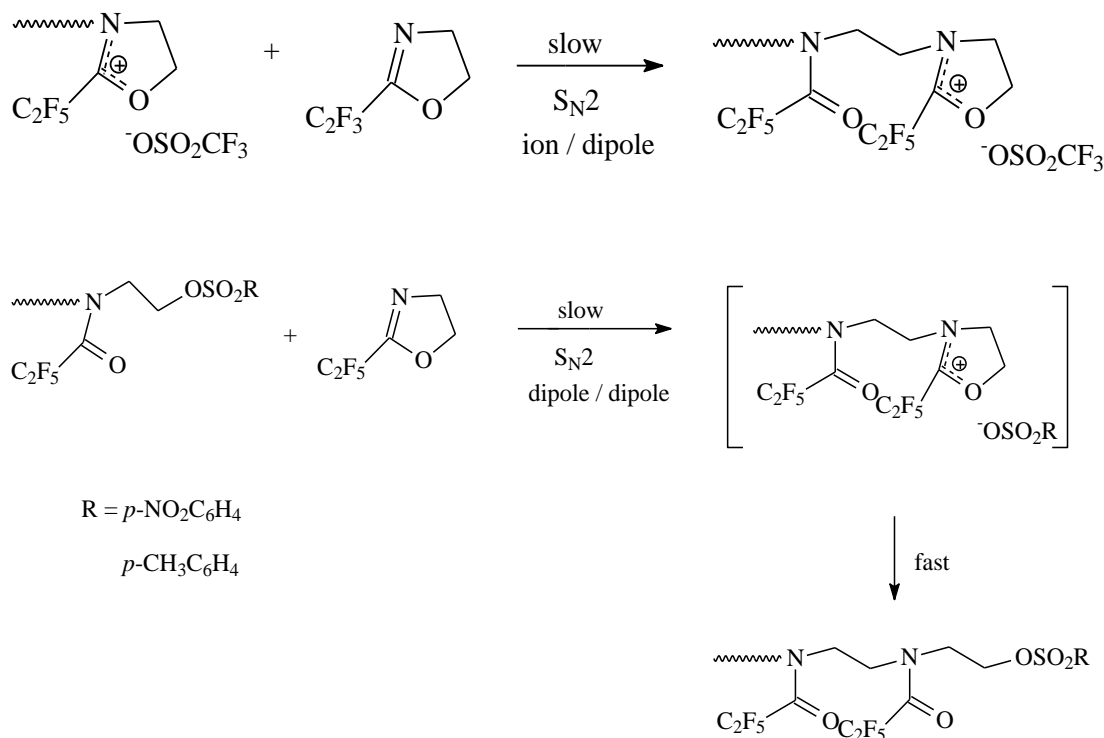
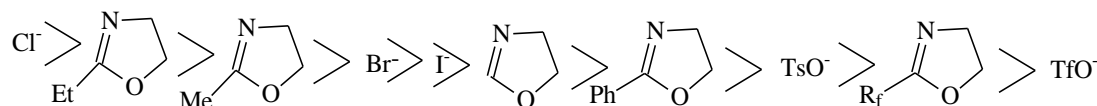


Figure 2.2. Mechanisms of electrophilic polymerization of 2-(perfluoroalkyl)-2-oxazoline with alkyl sulfonates

On the other hand, with methyl trifluoromethanesulfonate (MeOTf) initiator, which gives the more stable (less nucleophilic) triflate anion, propagation, proceeded through an ionic mechanism. These mechanisms were confirmed by three major experiments: (a) the *in situ*  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectroscopies of the polymerization systems, (b) the isolation of model compounds of propagating ends, i.e. 1:1 the adducts between 2-(perfluoro)-2-oxazolines and each of the initiators, and (c) kinetic studies on polymerization systems to determine the activation parameters. The conventional polymerizations of 2-oxazolines with sulfonates proceed exclusively via ionic species. However, the introduction of strong electron-withdrawing perfluoro-alkyl substituents changes this mechanism drastically.

Growing species in the polymerization of several 2-oxazolines have been examined with benzyl chloride, with methyl iodide, with MeOTs, and with MeOTf as initiators [11], [18].

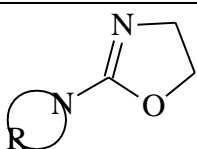
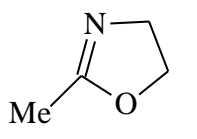
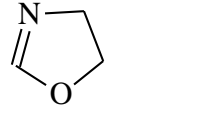
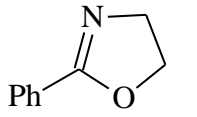
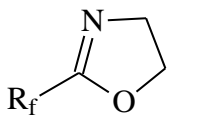
The results are summarized in Table 2.1, together with the case of DIP of 2-amino-2-oxazolines [13], [14]. The monomers and counteranions are placed by considering the order of nucleophilicities. Concerning the nature of propagating species in the polymerization of 2-oxazolines, the above monomers and counteranions are arranged in the following order of nucleophilicity where the concentration is not considered.



Ionic and covalent polymerization mechanisms are explained by the balance of nucleophilicities between monomers and counteranions. DIP of 2-amino-2-oxazolines is out of this relationship; since the propagation involves additional isomerization mechanisms.

A change in the type of propagating species was found for 2-ethyl-2-oxazoline polymerization with benzyl iodide or 1-iodobutane as the initiator in chlorobenzene (Figure 2.3.) [19]. NMR data suggested conversion of active covalent species to ionic species during the early course of the polymerization. This polymerization system was reported to be free of chain transfer as evidenced by a linear relationship between monomer conversion and number-average molecular weight determined by SEC in a 75/15(v/v) THF/MeOH mixture. However, the molecular weight distributions ( $M_w/M_n$  ca. 1.3, for benzyl iodide initiator system) for these polymers were broader than a Poisson distribution. Smaller initiation and initial covalent propagation rate constant than subsequent ionic propagation rate constant were derived. For example, these values are 0.00033, 0.00018, and 0.000079 L/mol-s, respectively, for the polymerization of 2-ethyl-2-oxazoline with benzyl iodide in chlorobenzene- $d_8$  at 80 °C.

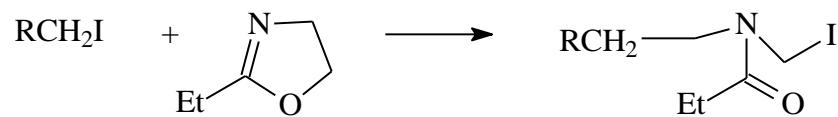
Table 2.1. Types of Propogating species in the polymerization of 2-oxazolines

Monomers		Counteranions, X <sup>-</sup>				References
		Nucleophilicity				
		←				
		Cl <sup>-</sup>	I <sup>-</sup>	TsO <sup>-</sup>	TfO <sup>-</sup>	
Nucleophilicity ↑		ionic and covalent (DIP)	ionic and covalent (DIP)	ionic	ionic	13,14
		covalent	ionic	ionic	ionic	15,16
		covalent	covalent	ionic	ionic	17
		-	covalent	ionic	ionic	18
		-	covalent	covalent	ionic	11,12

R<sub>f</sub> = C<sub>2</sub>F<sub>5</sub>, C<sub>3</sub>F<sub>7</sub>

The polymerization of 2-alkoxy-2-oxazoline (3) i.e. 2-ethoxy-2-oxazoline (8), with MeOTf gave a new class of polyoxazoline, poly[N-ethoxycarbonyl]ethylen-imine (12), in high yield, although the degree of polymerization was around 10 due to a chain transfer reaction involving the 2-ethoxy substituent of the propagating species [9]. The polymerization proceeded even at 0 °C in aprotic polar solvents. This is in contrast to the fact that the polymerizations of 2-oxazolines require a temperature above ca. 40 °C.

### Initiation



### Propagation

$m \geq 1$ ,  $n > m$ , R= Pr, for 1-iodobutane or Ph, for benzyl iodide

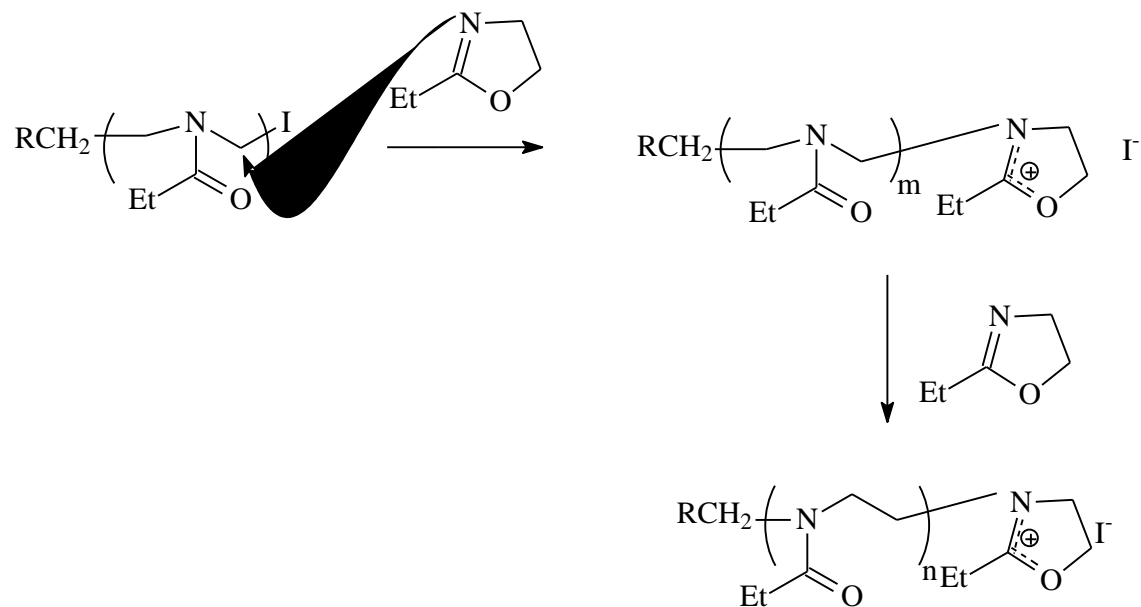
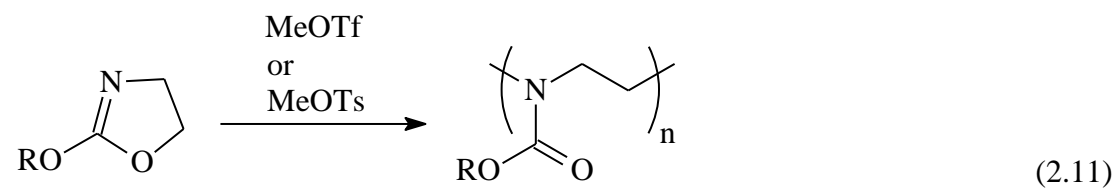


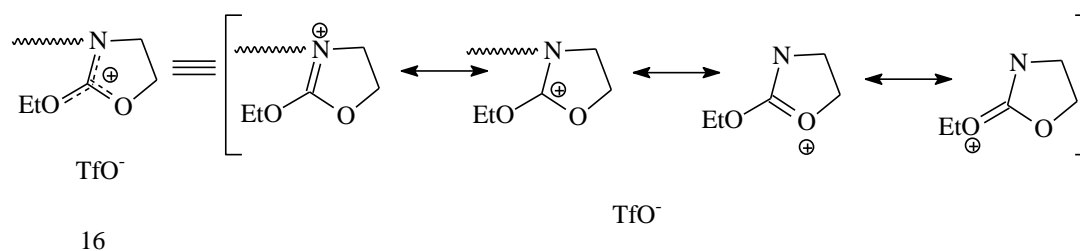
Figure 2.3. Mechanisms for polymerization of 2-ethyl-2-oxazoline with alkyl iodide in chlorobenzene



8, R=Et  
9, R=i-propyl  
10, R=cyclohexyl  
11, R=neopentyl

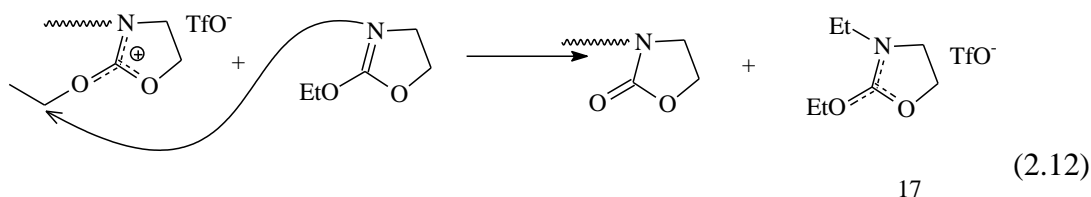
12, R=Et  
13, R=i-propyl  
14, R=cyclohexyl  
15, R=neopentyl

The propagation was proved to be an S<sub>N</sub>2-type propagating species 16. The cationic charge on the active species is stabilized by the contribution of the four tautomers. The contributions of the first three tautomers-ammonium, carbenium ion, and *endo*-oxonium-type ones-are common to those in 2-alkyl-2-oxazolinium salts. The additional contribution of the fourth *exo*-oxonium-type tautomer affords an extra reactivity.



The chain transfer mechanism is shown below. Nucleophilic attack of the monomer to the methylene carbon of the 2-ethoxy group of the propagation species results in the formation of 2-oxazolidone unit at the terminating end. The resulting 3-ethyl-2-ethoxy-2-oxazolinium triflate (17) re-initiates the polymerization, which forms a polymer having *N*-ethyl substituents at the initiating end. This chain-transfer reaction is unique to 2-alkoxy-2-oxazoline.

#### Chain-transfer



For the polymerizations of 2-*i*-propyloxy- (9) and 2-cyclohexyloxy-2-oxazoline (10) having secondary alkyl substituents, the contributions of chain-transfer is minor. Chain transfer is suppressed in the polymerization of 2-oxazoline having a bulky alkoxy group, 2-(neopentyloxy)-2-oxazoline (11). A polymer 15 with relatively narrow molecular weight distributions ( $M_w/M_n < 1.2$ ) was obtained from 11.



## 2.3. Photolatent System

### 2.3.1. Onium Salts

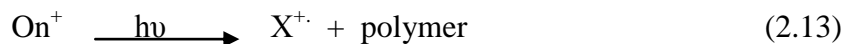
Onium salts are the most widely used cationic photoinitiators. These salts are compounds containing heteroatom, with a cationic center on the heteroatom. As counterions, mostly inorganic metal complex anions are used. The onium salts were used for light induced cationic polymerization.

Regarding pyridinium salts, the classification as onium salts has been the subject of controversy. However, since the chemistry of these salts resembles that of classical onium salt initiators, such as iodonium and sulphonium salts, it will be treated as an onium salt in this review.

The polymerization by onium salts does generally start only after an external stimulation such as irradiation or heating. However, in a few cases dark polymerizations at room temperature have been observed.

#### 2.3.1.1. Direct Photolysis

Onium salts generate initiating species upon photolysis at appropriate wavelengths. In general, radical cations were found to be the primary species and play key role for the initiation.



Two different mechanisms were proposed. Radical cations are highly reactive towards monomers and can directly initiate the polymerization.

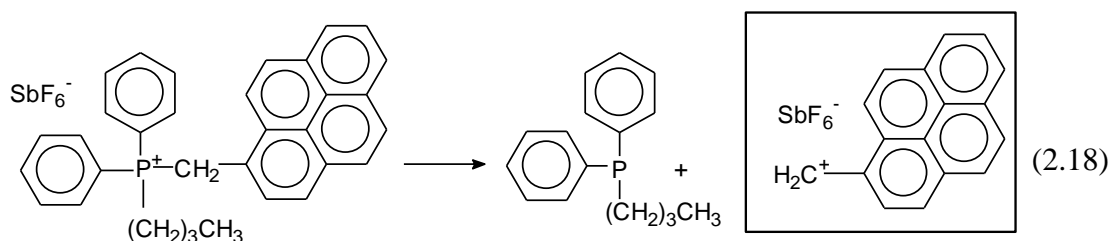


Alternatively, protons generated by hydrogen abstraction of radical cations can add to monomers.



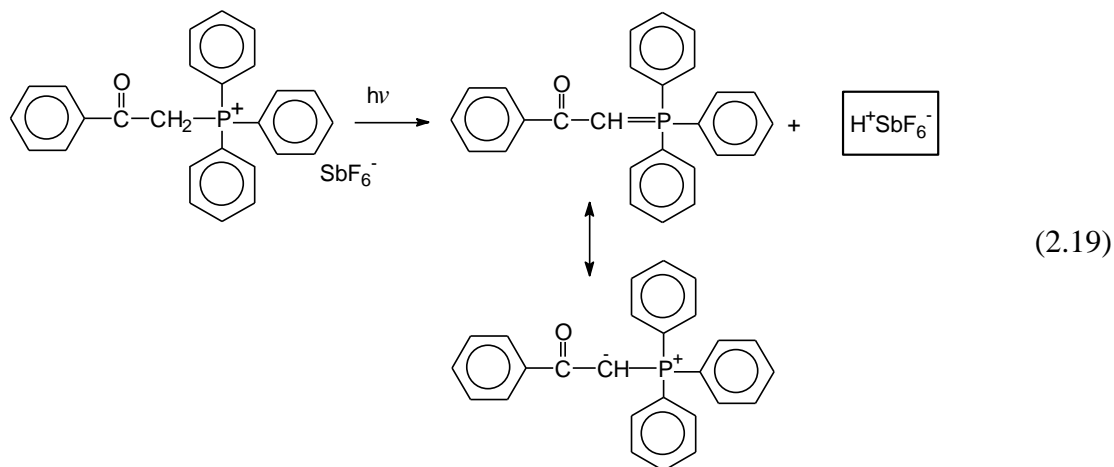
### 2.3.1.1.1. Phosphonium Salts

The preparation of phosphonium salts is based on the reaction of chloromethylated or bromomethylated aryl compounds with the corresponding phosphines [21]-[23]. Benzyl or pyrenylmethyl group containing phosphonium salts produce the respective carbon centered cations after a heterolytic bond rupture according to (2.18) [24]-[26]. These cations are assumed to be the initiating species in cationic polymerization.



The excellent initiating ability of phosphonium salts containing pyrenylmethyl groups has been demonstrated for epoxides and vinyl monomers [26], [27].

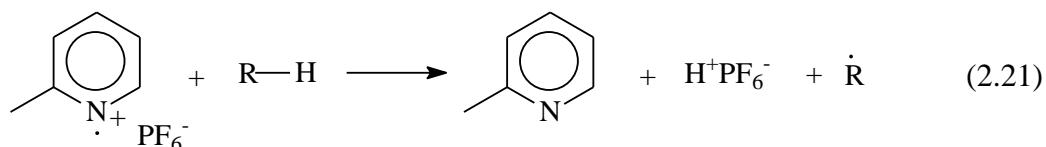
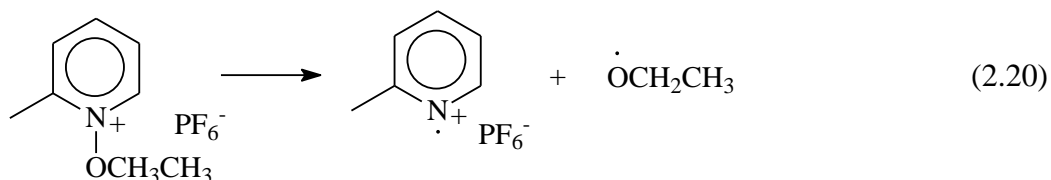
In the case of phenacyltriphenyl phosphonium salts, however, Brønsted acid is expected to initiate cationic polymerizations. Upon photolysis of these salts, the resonance stabilized ylide and protons are formed. Phenacyltriphenyl phosphonium salts were used for the cationic polymerization of cyclohexene oxide [23], [29] styrene [30] and *p*-methyl styrene [28].



### 2.3.1.1.2. N-Alkoxy Pyridinium Salts

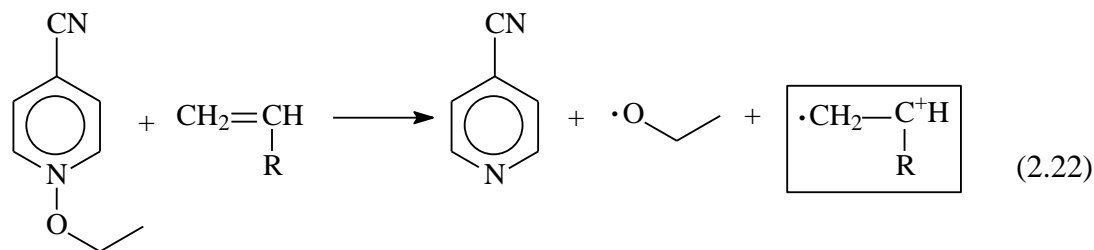
A reaction of pyridine N-oxides with a triethoxonium salt in methylene chloride results in N-alkoxy pyridinium salts [31]. Quinolinium salts are obtained from N-oxides [32]. Since the triethyl oxonium salt is available with non-nucleophilic counter anions, an anion exchange is not necessary in both cases.

As depicted in eqns (2.20) and (2.21) for N-ethoxy-2-methylpyridinium hexafluorophosphate ( $\text{EMP}^+\text{PF}_6^-$ ), a pyridinium type radical cation and an alkoxy radical are formed as a result of the initiator's nitrogen-oxygen bond rupture. According to the laser flash photolysis detection, reactivity of the radical cation towards various nucleophilic monomers was found to be very high.



In the presence of hydrogen donors (monomer, solvent), Brønsted acid is produced and it initiates polymerization as the radical cation.

In a recent study, Zhu and Schnabel [34] have reported dark polymerization with  $\text{EMP}^+$ , N-ethoxy-4-cyanopyridinium ( $\text{EPP}^+$ ) and N-ethoxyisoquinolinium ( $\text{EIQ}^+$ ) salts. The  $\text{EMP}^+$  does not initiate the polymerization reaction in dark while the others polymerize isobutylvinylether and N-vinylcarbazol without any irradiation. In contrast, no dark polymerization of cyclohexene oxide was observed for any of the three salts. The mechanism proposed for explaining the dark polymerization involves an electron transfer from monomer to the onium salt. The initiation may be generated by monomer based cation.



### 2.3.1.2. Indirect Photolysis

Onium salts used in cationic photopolymerization mainly absorb the wavelengths of light between 225 and 350 nm [31], [35], [36]. Since this requirement is not fulfilled for certain easily available onium salts several systems were developed to extend the applicability of the onium salt photoinitiators. One possible pathway in tackling this dilemma is the chemical attachment of chromophoric groups to the onium salt making it absorb at higher wavelengths. Besides, additives are present which participate in the reaction sequence to yield reactive species capable of initiating the cationic polymerization. At the wavelength chosen for the polymerization, the onium salt initiator is virtually transparent. Incident light is almost entirely absorbed by the additive. Thus, provided the systems obtained do initiate cationic polymerizations.

## 2.4. Thermolatent System

In many curing applications, the hardening of monomer containing curing formulas by heat is desired. Regarding radical polymerization, a large number of initiating thermolabile compounds is known, which contain mostly either azo or peroxide groups. One can cure coatings at virtually any temperature desired by choosing the appropriate initiator compound.

As far as cationic polymerization is concerned, it has to be said that some of the onium salts may be activated thermolytically, too. However, mostly onium salts with slight differences in the pattern of substitution are used. For example, for photoinitiation N-alkoxy pyridinium salts serve as initiators whereas for thermal polymerization, N-benzyl

pyridinium salts are utilized. Besides the direct thermolysis of the initiator, also indirect methods which are similar have been reported. Thermally generated radicals can be used in radical oxidation and addition fragmentation schemes for producing appropriate initiating cations.

Concerning energy absorption, thermal and photolytical initiations differ for the following: in the case of thermal initiation, all chemical bonds absorb energy, whereas for photoinitiation, the photon energy is absorbed only by suitable chromophoric groups. For cationic photoinitiators, much effort has been made to introduce chromophoric groups absorbing at high wavelengths into the molecule or to use additives containing appropriate chromophores. In contrast to this, for thermal cationic initiators, research has been devoted to chemical groups that undergo the bond rupture desired to a sufficient extent at relatively low temperature. The initiating compounds have however to be stable at room temperature; otherwise their thermal latency would be lost.

As described in this section, initiators suitable for an application at various temperature ranges are available. Approaches to overcome the solubility problem often observed with onium salts are also described.

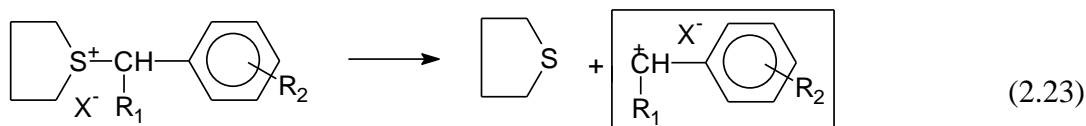
### **2.4.1. Direct Thermolysis**

#### **2.4.1.1. Sulphonium Salts**

Sulphonium salts have a considerable potential as cationic *photoinitiators*. This refers, however, only to triarylsulphonium salts. Alkyl substituted sulphonium salts are thermally unstable, decomposing sometimes already at room temperature. The reason, why alkylsulphonium salts are more thermally reactive than arylsulphonium salts is that the former are stabilized only by hyperconjugation, whereas the latter by resonance.

Due to the stabilization of the leaving *benzyl cation* by resonance, alkyl*benzyl*sulphonium and alkylaryl*benzyl*sulphonium salts possess a high thermal sensitivity.

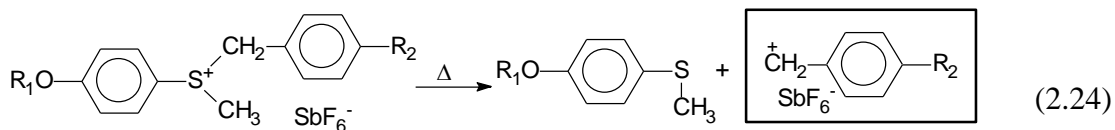
The synthesis of *benzylthiophenium salts* is achieved through a reaction of respectively substituted benzylhalides with tetrahydrothiophene and a subsequent anion exchange. As confirmed by NMR analyses of polymer formed [37], the initiating species are thermolytically generated benzyl cations.



Regarding the effect of the substituent in the aromatic ring,  $R_2$ , it turned out clearly that electron donating substituents enhance the initiation activity by stabilizing the benzyl cation evolved. For example, with the  $p\text{-OCH}_3$  derivative, for a 50% conversion in styrene polymerization  $50^\circ\text{C}$  were sufficient whereas with the unsubstituted derivative, as much as  $120^\circ\text{C}$  had to be applied for obtaining the same conversion in the same time (30 min) [37]. Besides for styrene, benzylthiophenium salts have been used for polymerizing spiroorthocarbonates [38], bifunctional epoxides [39], [40] and mesogenic vinyl ethers [41], [42].

*p*-Methoxybenzylalkylsulphonium salts are synthesized by a reaction of the corresponding sulfides with *p*-methoxybenzylbromide [43]. The thermal reactivity of these substances, which release benzyl cations, was found to drop in the order  $\text{C(CH}_3\text{)}_3 > (\text{CH}_2)_2\text{CH}_3 > \text{CH}_2\text{CH}_3 > \text{CH}_3$ . This order has been explained in terms of the substituent's bulkiness: the more bulky the substituent, the smaller is the number of ion pair recombinations after the ions have diffused out of the solvent cage.

Other highly thermosensitive benzylsulphonium salts are *benzyl phenylalkyl sulphonium salts* [44], [45], [46]. These salts are obtained by a reaction of correspondingly substituted phenylsulfides with benzylchloride and dimethylsulfate. In this case, benzyl cations have been shown to initiate the polymerization.



As far as the substituents in the benzyl group,  $R_2$ , are concerned, electron donating substituents were found to enhance the thermal sensitivity by stabilizing the benzyl cation. The reactivity diminishes in the order  $\text{CH}_3 > \text{H} > \text{Cl} > \text{NO}_2$  [46]. The temperature necessary to obtain a 50% conversion in the bulk polymerization of glycidylphenylether within 1h, varies from 60°C ( $R_2=\text{CH}_3$ ) to 120°C ( $R_2=\text{NO}_2$ ). Regarding phenyl ring substituents,  $R_1$ , electron withdrawing groups were found to increase the thermal sensitivity due to the destabilization of the sulfur centered cation. In the case of the *p*- $\text{CH}_3\text{OC}(\text{O})\text{O}$  derivative (strong -I effect), polymerizations were initiated even at room temperature. Notably, no difference in activity between OH and  $\text{OCH}_3$  derivatives was found, thus confirming that the possible formation of protons by the cleavage of the O-H bond is of no importance regarding the initiation. Instead, the initiation is also in this case due to benzyl radicals. The comparison with the phenyldimethylsulphonium salt [46] revealed clearly the importance of the benzyl group for thermal sensitivity. In the case of the benzyl free sulphonium salt, bulk polymerizations of phenyl glycidyl ether were observed only at temperatures above 150°C, whereas for the benzyl containing derivative (unsubstituted benzyl group), 90°C were fully sufficient.

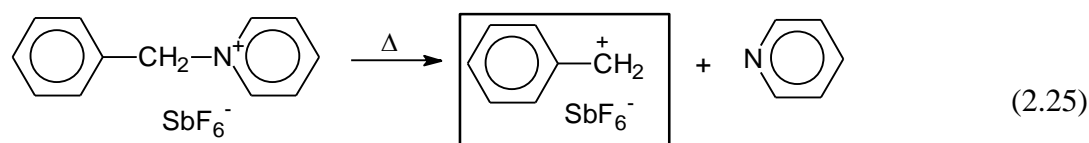
#### **2.4.1.2. N-Containing Onium Salts**

##### **2.4.1.2.1. Benzyl Pyridinium Salts**

*N-Benzyl pyridinium salts*, the N-containing onium salts most frequently used for thermal cationic polymerization [55], are facile to prepare by reacting benzyl chlorides with corresponding pyridines [47]. That reaction yields pyridinium salts possessing nucleophilic chloride anions. Therefore, the counter anion has to be exchanged for a less nucleophilic one. The N-benzyl pyridinium salts have so far been used for thermal induced cationic polymerization.

N-benzyl pyridinium salts were successfully applied for the polymerization of cyclic and vinyl monomers. It was found that they possess a much better thermal initiation ability than aliphatic ammonium salts. This is, undoubtedly due to the low bond energy of benzylic C-N bond giving rise to bond ruptures at moderate temperatures. The reaction

mechanism that has been evidenced by the chemical analysis of obtained polymer [48] is depicted in (2.24).

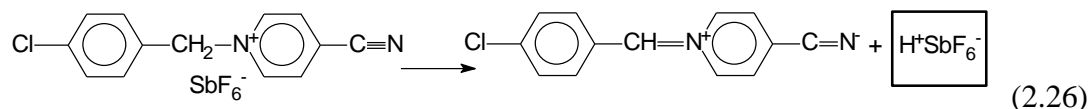


The *substituents in the pyridinium ring* exert a strong effect on the activity of these salts. The *p*-CN substituted benzyl pyridinium salt has often been used for cationic polymerizations. It is more reactive than unsubstituted N-benzyl pyridinium, but suffers from the disadvantage of still requiring high temperatures for a successful polymerization (>100°C) [47], [48]. Other analogs with *p*-substituents in the pyridinium moiety show a worse performance in cationic polymerization. The activity for pyridinium ring *p*-substituents was found to decrease in the order *p*-CN > H > *p*-CH<sub>3</sub> > *p*-N(CH<sub>3</sub>)<sub>2</sub>. This order indicates that electron accepting groups stabilize the cation on the pyridinium N-atom thereby diminishing the leaving ability of the pyridinium moiety [49]. If the pyridinium ring is substituted by *o*-CN instead of *p*-CN, the thermal sensitivity is drastically improved, increasing the activity by a factor of 20 to 30 [50]. The effect of the *o*-CN substituent was attributed to both steric and electronic factors.

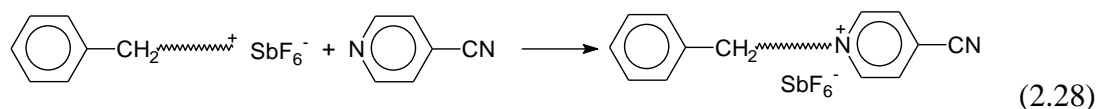
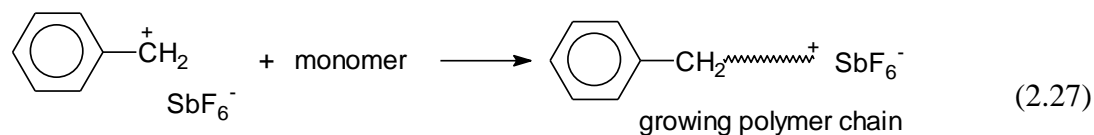
The *substitution of the benzene ring* by electron donating groups stabilizes the benzyl cation formed thermolytically thus further enhancing the thermal activity. The activity of pyridinium salts with various *p*-substituents at the benzene ring falls in the order CH<sub>3</sub>O > Cl > *t*-C<sub>4</sub>H<sub>9</sub> > CH<sub>3</sub> > H [51]. Notably, if the benzene ring is substituted by CH<sub>3</sub>O, the thermal latency may be lost: with *p*-methoxybenzyl *o*-cyanopyridinium, polymerizations are observed already at room temperature [52]. The relatively high activity of N-benzyl pyridinium salts substituted with electron withdrawing *p*-Cl groups at the benzene ring has been attributed to the occurrence of side reactions like the formation of ylide and Brønsted acid. The latter acts as an additional cationically initiating species. In the case of *p*-Cl substituted N-benzyl pyridinium salts, IR and <sup>1</sup>H-NMR measurements of the polymers obtained gave no evidence for the presence of benzyl moieties in the polymer. Thus it has been confirmed that the initiating species are protons rather than benzyl



cations. For other N-benzyl pyridinium salt, the incorporation of benzyl groups into the polymer has been proven by chemical analysis [53].



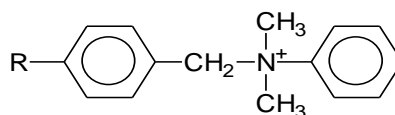
It has to be pointed out that the substituted or unsubstituted pyridine liberated in the course of decomposition of N-benzyl pyridinium salts (see (2.24)) plays a significant role in the propagation step. Pyridine is a relatively strong base, which is potentially able to react with the cationic chain ends. The basicity of pyridine's N-atom is enhanced by electron withdrawing groups, such as CN. Thus, after adding additional *o*-cyanopyridine or *p*-cyanopyridine to the polymerization mixtures, the bulk and solution polymerization of glycidyl phenylether was strongly suppressed, indicating the interaction of pyridine moiety with propagating chain ends [49]. NMR studies of the polymerization mixture in which propylene oxide was used as a monomer, revealed that this interaction is weaker for *o*-cyanopyridine than for *p*-cyanopyridine. The role of pyridine in the propagation is illustrated as follows.



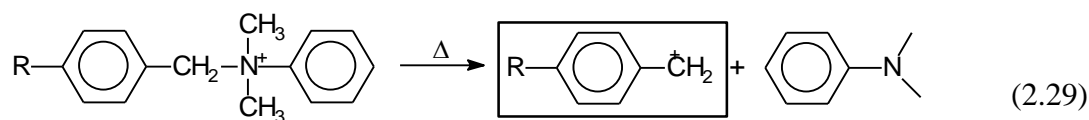
#### 2.4.1.2.2. Other N-containing Onium Salts

Besides N-benzyl pyridinium salts, further salts with positively charged nitrogen atoms have been utilized as thermolatent cationic initiators.

Recently, the thermal initiation by benzyl ammonium salts having the following general structure, with R = OCH<sub>3</sub>, *t*-C<sub>4</sub>H<sub>9</sub>, CH<sub>3</sub>, Cl, were investigated in detail [51].



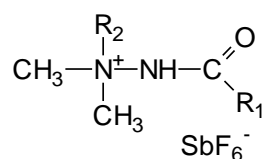
These salts may be conveniently synthesized by reacting the corresponding benzyl chlorides with N,N-dimethylaniline in acetonitrile. The thermolysis of benzyl ammonium salts gives tertiary ammonium and benzyl cations, the latter being very efficient in initiating cationic polymerizations.



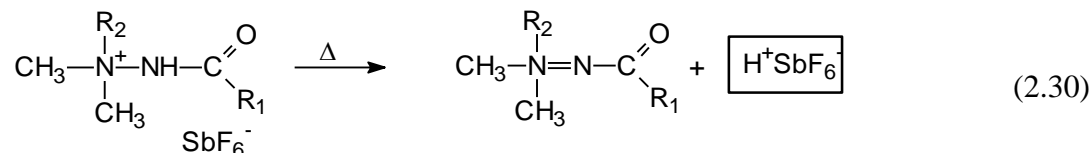
The initiator properties of these salts were demonstrated upon polymerizations of glycidyl phenyl ether. The yield with which initiating cations are formed falls in the order  $\text{CH}_3\text{O} > t\text{-C}_4\text{H}_9 > \text{CH}_3 > \text{Cl}$ , what is explainable in terms of the stabilization of ensuing benzyl radicals by electron donating groups. For example, with the methoxy derivative, 10 min heating at  $100^\circ\text{C}$  yielded 30% monomer conversion, whereas for the chlorine derivative,  $190^\circ\text{C}$  had to be applied in order to reach the same conversion within the same time period.

Notably, benzyl ammonium salts are more efficient initiators than the analog N-benzyl pyridinium salts with the same substituents. This efficiency has been assigned to steric reasons. The benzylammonium salts are expected to have a greater steric hindrance between the benzyl group and the ammonium moiety compared to N-benzyl pyridinium salts. This steric hindrance accounts for fewer recombinations, provided the species formed manage to diffuse out of the solvent cage.

Hydrazinium salts have been introduced recently as thermally latent Brønsted acid generating initiators [53]. Various salts of the common structure



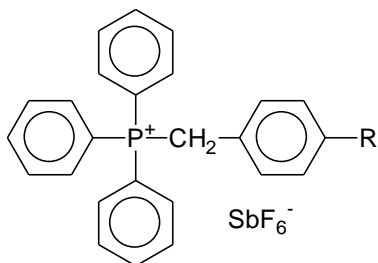
with  $R_1 = \text{CH}_3$ ,  $\text{C}_6\text{H}_5$ ,  $p\text{-NO}_2\text{-C}_6\text{H}_4$  and  $R_2 = \text{C}_6\text{H}_5\text{CH}_2$ ,  $p\text{-CH}_3\text{O-C}_6\text{H}_4\text{CH}_2$ ,  $\text{CH}_3$ , have been prepared by reacting 1,1-dimethylhydrazine with the acid chloride containing  $R_1$  and the chlorine derivative of  $R_2$ . After the reaction, the anions were exchanged. Upon heating, these salts release initiating protons, most probably according to



The evaluation of the initiator activity in glycidyl vinyl ether polymerization revealed that the  $p\text{-NO}_2\text{-C}_6\text{H}_4$  substituent ( $R_1$ ) is most effective in increasing the thermal sensitivity. With initiators containing this substituent, polymerizations were performed at  $50^\circ\text{C}$ .

#### 2.4.1.3. Phosphonium Salts

Substituted benzylphosphonium salts of the general structure with R being  $\text{NO}_2$ , Cl, H,  $\text{CH}_3$ ,  $\text{OCH}_3$ , have been synthesized by the reaction of correspondingly substituted benzyl chlorides with triphenylphosphine. In a second reaction step, the counter anion has been exchanged for the low nucleophilic  $\text{SbF}_6^-$  [54]. These salts have been used for the thermal polymerization of glycidyl phenyl ether and cyclohexene oxide at temperatures in the range between  $100$  and  $170^\circ$  [25], [26].



Interestingly, the activity of these compounds was found to *raise* with changing for more electron withdrawing substituents; the order of reactivity observed is  $\text{OCH}_3 < \text{CH}_3 < \text{H} < \text{Cl} < \text{NO}_2$ . This is sharp contrast to benzyldisulphonium and benzylpyridinium salts, where electron withdrawing substituents *reduced* the thermal sensitivity by destabilizing the

$$\begin{array}{c}
 \text{Ph}_3\text{P}^+-\text{CH}_2-\text{Ph}-\text{R} \\
 \text{SbF}_6^-
 \end{array}
 \longrightarrow
 \begin{array}{c}
 \text{Ph}_3\text{P}^+-\text{CH}^--\text{Ph}-\text{R} \\
 \text{H}^+\text{SbF}_6^-
 \end{array}
 + \text{H}^+\text{SbF}_6^-
 \rightleftharpoons
 \begin{array}{c}
 \text{Ph}_3\text{P}=\text{CH}-\text{Ph}-\text{R}
 \end{array}
 \quad (2.31)$$

### **3. EXPERIMENTAL WORK**

#### **3.1 Materials and Chemicals**

##### **3.1.1 Monomer**

###### **2-Ethyl-2-oxazoline**

2-Ethyl-2-oxazoline (EOZO) used as monomer, was a product of Merck. It was purified by distillation and stored over molecular sieves.

##### **3.1.2 Solvents**

###### **Acetone [(CH<sub>3</sub>)<sub>2</sub>CO] (J.T.Baker)**

Acetone [(CH<sub>3</sub>)<sub>2</sub>CO], used as solvent in the synthesis of salts, was a product of J.T.Baker. It was purified by distillation before used.

###### **Acetonitrile (CH<sub>3</sub>CN) (J.T.Baker)**

Acetonitrile (J.T.Baker) was used as solvent in polymerization, dilution of polymer solutions. It was also used as solvent in the synthesis of salts. It was purified by distillation before used.

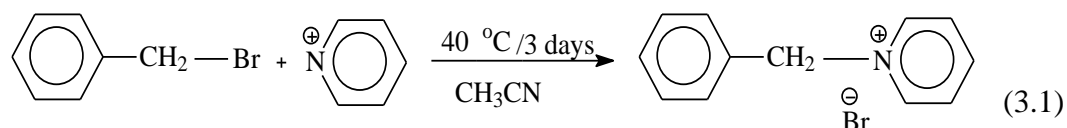
###### **Anhydrous diethyl ether [(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O] (J.T.Baker)**

Anhydrous diethyl ether (J.T.Baker) was used as a solvent for the precipitation of polymers.

### 3.1.3 Cationic Initiators

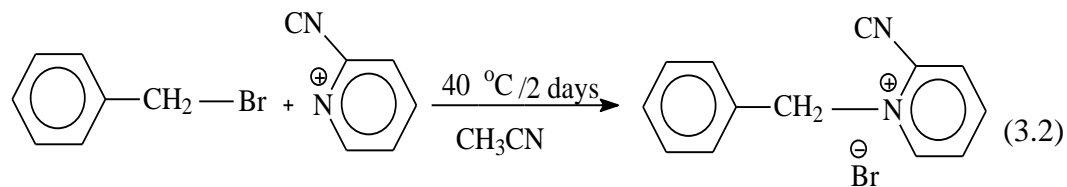
#### 3.1.3.1 Synthesis of *N*-Benzyl pyridinium bromide (I) (BPyBr)

A mixture of benzyl bromide (3.6 mL, 30 mmol), pyridine (2.5 mL, 30 mmol) and 1.23 g (1.56 mL) of acetonitrile was stirred and maintained at 40 °C for 3 days. After acetonitrile was removed under vacuum, acetone (40 mL) was poured into the mixture to isolate the white bromide salt by filtration, washed copiously with diethyl ether and dried (yield, 83 %). <sup>1</sup>H-NMR (D<sub>2</sub>O, ppm) δ 5.80 (s, 2H, CH<sub>2</sub>), 7.48 (s, 5H, Ph), 8.02-8.08 (t, 2H, Py), 8.51-8.57 (t, 1H, Py), 8.89-8.91 (d, 2H, Py)



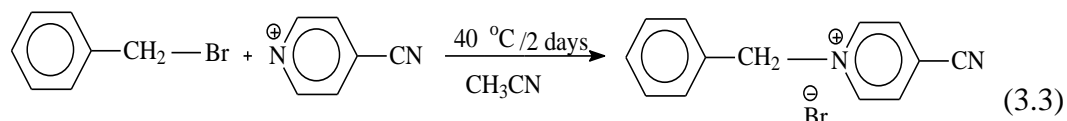
#### 3.1.3.2 Synthesis of *N*-Benzyl-*o*-cyanopyridinium bromide (II) (B-*o*-CNPyBr)

A solution of benzyl bromide (3.6 mL, 30 mmol), and *o*-cyanopyridinium (1.56 g, 15 mmol) was stirred and maintained at 40 °C for 2 days. Acetone (40 mL) was poured into the mixture to isolate the light green bromide salt by filtration, washed copiously with diethyl ether and dried (yield, 77.5 %), m.p.: 140 °C <sup>1</sup>H-NMR (D<sub>2</sub>O, ppm) δ 6.10 (s, 2H, CH<sub>2</sub>), 7.49 (s, 5H, Ph), 8.35-8.38 (d, 1H, Py), 8.64-8.80 (m, 2H, Py), 9.15-9.18 (d, 1H, Py).



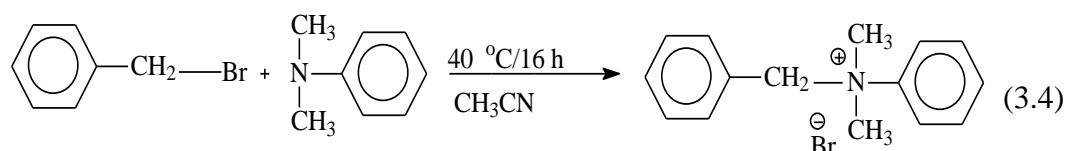
### 3.1.3.3 Synthesis of *N*-Benzyl-*p*-cyanopyridinium bromide (III) (B-*p*-CNPyBr)

A mixture of benzyl bromide (3.6 mL, 30 mmol), and *p*-cyanopyridinium (1.56 g, 15 mmol) was stirred and maintained at 40 °C for 2 days. Acetone (40 mL) was poured into the mixture to isolate the white bromide salt by filtration, washed copiously with diethyl ether and dried (yield, 80 %), m.p.: 205 °C <sup>1</sup>H-NMR (D<sub>2</sub>O, ppm) δ 5.94 (s, 2H, CH<sub>2</sub>), 7.53 (s, 5H, Ph), 8.49 (s, 2H, Py), 9.18-9.21 (d, 2H, Py).



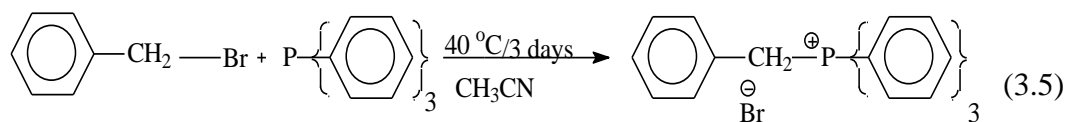
### 3.1.3.4 Synthesis of *N*-Benzyl-*N*, *N*-dimethylanilinium bromide (IV) (BDMABr)

A mixture of benzyl bromide (3.6 mL, 30 mmol), *N,N*-dimethylaniline (3.8 mL, 30 mmol) and 1.23 g (1.56 mL) of acetonitrile was stirred and maintained at 40 °C for 16 hours. After acetonitrile was removed under vacuum, acetone (20 mL) was poured into the mixture to isolate the green bromide salt by filtration, washed copiously with diethyl ether and dried (yield, 90 %), m.p.: 160 °C <sup>1</sup>H-NMR (D<sub>2</sub>O, ppm) δ 3.65 (s, 6H, 2CH<sub>3</sub>), 4.97 (s, 2H, CH<sub>2</sub>), 7.05-7.08 (d, 5H, Ph), 7.31-7.37 (t, 1H, Ph), 7.46-7.51 (t, 2H, Ph), 7.62 (s, 2H, Ph).



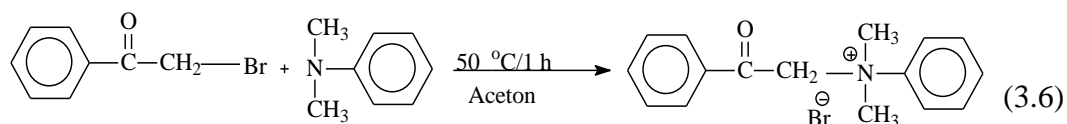
### 3.1.3.5 Synthesis of *N*-Benzyl-triphenyl phosphonium bromide (V) (BTPhPBr)

A mixture of benzyl bromide (0.6 mL, 5 mmol), triphenylphosphine (1.32 g, 5 mmol) was stirred and maintained at 40 °C for 3 days. After acetonitrile was removed under vacuum, the white bromide salt was isolated by filtration, washed copiously with diethyl ether and dried (yield, 75.6 %), m.p.: 310 °C <sup>1</sup>H-NMR (D<sub>2</sub>O, ppm) δ 6.97-7.00 (d, 2H, CH<sub>2</sub>), 7.23-7.26 (d, 5H, Ph), 7.55-7.88 (m, 15H, 3Ph).



### 3.1.3.6 Synthesis of *N*-Phenacyl, *N,N*-dimethylanilinium bromide (VI) (PDMABr)

Into a 100 mL round bottom flask equipped with a magnetic stirrer and a reflux condenser was placed 0.75 g (3.77 mmol) of bromoacetophenone, 0.5 mL (3.77 mmol) *N,N*-dimethylaniline and 50 mL of acetone. The reaction mixture was brought to reflux and held at 50 °C for 1 hour. Acetone was removed under vacuum; the white bromide salt was isolated by filtration and dried. <sup>1</sup>H-NMR (D<sub>2</sub>O, ppm) δ 3.29 (s, 6H, 2CH<sub>3</sub>), 3.78 (s, 2H, CH<sub>2</sub>), 7.48-7.86 (m, 10H, 2Ph).



### 3.1.4 Other Chemicals

#### *N,N*-Dimethylaniline (Fluka) (%98)

*N,N*-dimethylaniline was a product of Fluka. It was distilled prior to use.

#### Bromoacetophenone (Fluka) (%98)

Bromoacetophenone was a product of Fluka and used as received.

#### Benzylbromide (Fluka) (%98)

Benzylbromide was a product of Fluka and used as received.



### **2-Cyanopyridine (Fluka) (%98)**

2-Cyanopyridine was a product of Fluka and used as received.

### **4-Cyanopyridine (Fluka) (%98)**

4-Cyanopyridine was a product of Fluka and used as received.

### **Pyridine (Fluka) (%99.5)**

Pyridine was a product of Fluka and used as received.

### **Triphenyl phosphin (Fluka) (% 99)**

Triphenyl phosphin was a product of Fluka and used as received.

## **3.2 Equipment**

### **3.2.1 Photoreactor**

For photoirradiations, Rayonet merry-go-round photoreactor equipped with 16 lamps emitting nominally at 300 and 350 nm were utilized.

## **3.3. Polymerization**

### **3.3.1 Thermal polymerization**

Monomer solutions in acetonitrile, in Pyrex tubes, containing given salt. Initiation was effected by placing the vessels in an oil bath at 105 °C for 6 hours. At the end of this time polymer was obtained by precipitation into anhydrous diethyl ether. Conversions were calculated gravimetrically.

### 3.3.2 Photopolymerization

Typical procedure. First, a solution of V (0.020 g, 0.06 mmol) or IV (0.026 g, 0.06 mmol) and EOZO (5 mL, 4.95 mmol) in 1.5 mL CH<sub>3</sub>CN was contained in quartz tube (i.d.= 9 mm) and filled with dry nitrogen prior to irradiation from Rayonet merry-go-round photo reactor equipped with 16 lamps emitting nominally at  $\lambda = 300$  nm. At the end of irradiation for six hours, polymers were precipitated in 10-fold excess anhydrous diethyl ether and dried in vacuum. Conversions for both samples were determined gravimetrically.

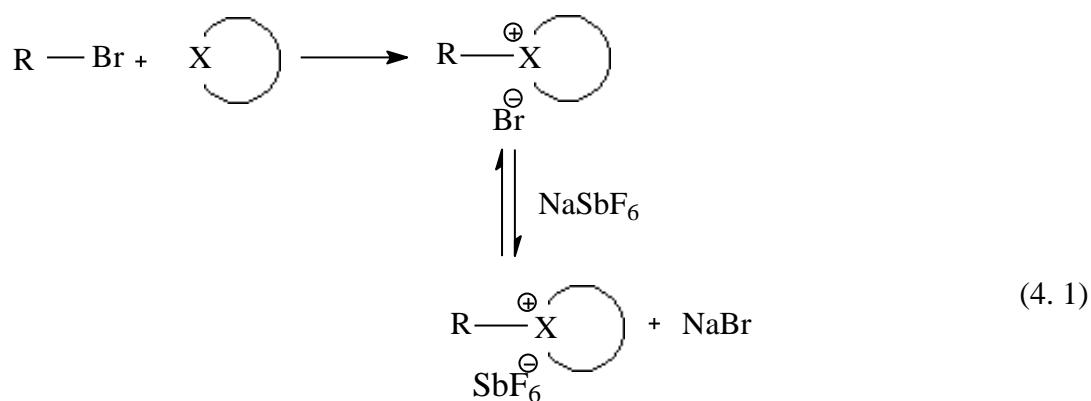
### 3.4 Characterization

GPC analyses of the polymers were performed at room temperature with a setup consisting of a pump (Waters 600E) and four Waters ultrastryragel columns: HR 5E (2000-4 - 10<sup>6</sup> g/mol), HR4 (5000-60 000 g/mol), HR3 (500-30 000 g/mol), and HR2 (500-20 000 g/mol). THF was used as the eluent (flow rate 1 mL min<sup>-1</sup>), and the detection was carried out with the aid of a Waters 410 differential refractometer. The number-average molecular weights were determined using Polymer Laboratories polystyrene standards. <sup>1</sup>H-NMR spectra were recorded on a Bruker 250 instrument with D<sub>2</sub>O and CD<sub>3</sub>CN as a solvent and tetramethylsilane (TMS) as the internal standard.

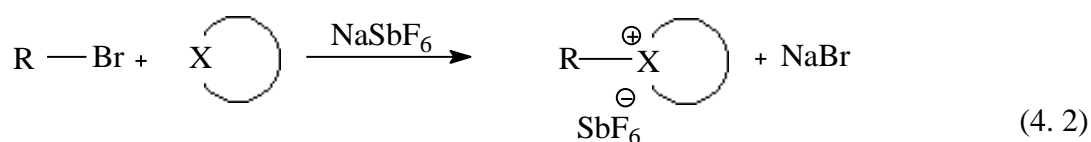
## 4. RESULTS and DISCUSSION

### 4.1 Synthesis and Characterization of the Salts

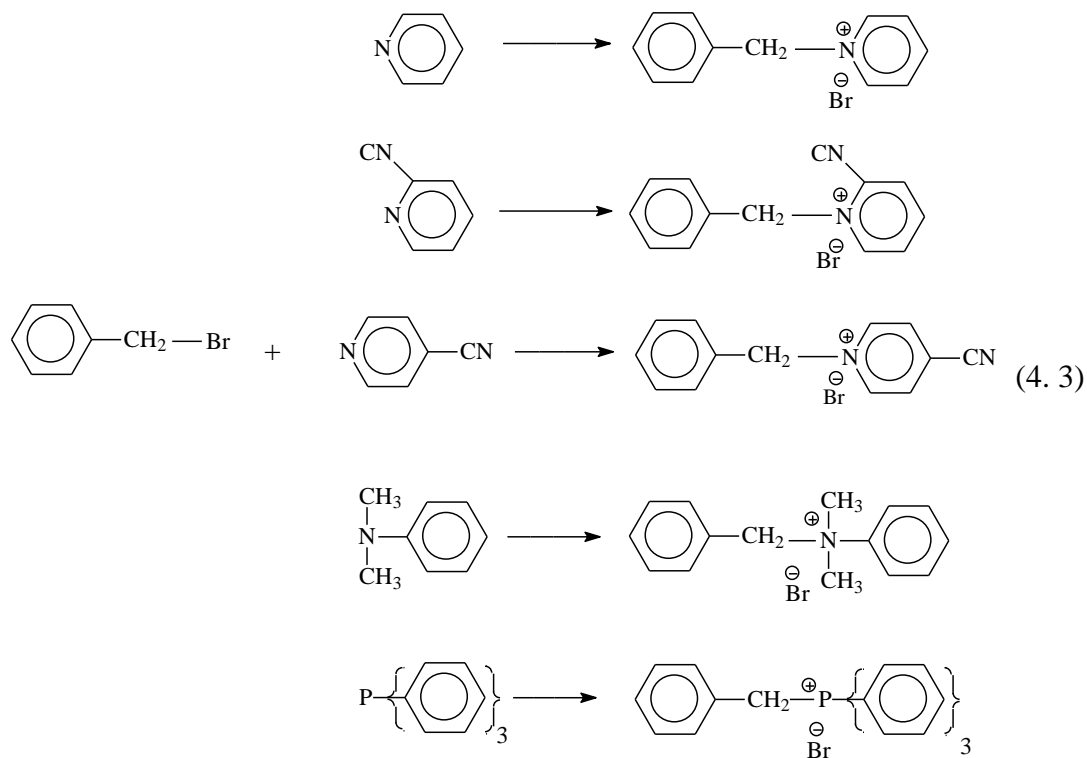
Although all of the salts reported in this work were synthesized previously, they were equipped with different non-nucleophilic counter anions such as  $\text{SbF}_6^-$  or  $\text{PF}_6^-$ . However, the salts with bromide counter anions were usually formed as an intermediate and directly converted to non-nucleophilic ones without isolation.



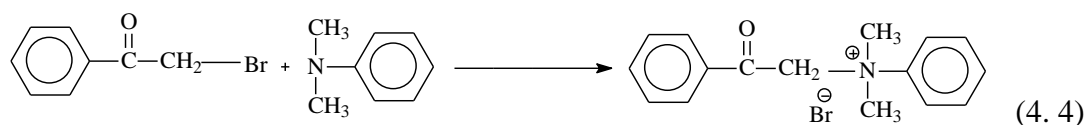
Alternatively, salts with non-nucleophilic counter anions were formed in a one-pot manner. In this case, the metathesis of the counter anion was achieved simultaneously. (X= Hetero atom)



Therefore, synthesis and characterization of the isolated salts with bromide anions were reported for the first time in this work. For our own purpose, the alkyl group was selected as benzyl or phenacyl group so as to facilitate the subsequent cationic polymerization.



Synthesis of thermally latent cationic salts.



Synthesis of photolatent cationic salts.

According to the spectral investigations the salts with desired structure were obtained.

Table 4.1. Benzylic protons appeared in  $^1\text{H}$ -NMR spectrum of the salts used.

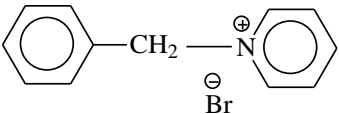
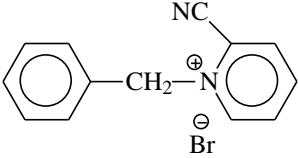
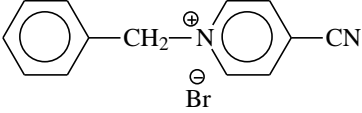
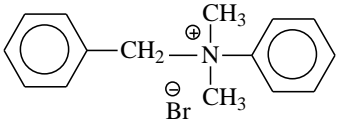
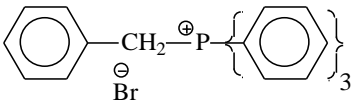
Salts	Aromatic Protons (ppm)	$\text{CH}_2$ Protons (ppm)
	7.48	5.80
	7.49	6.10
	7.53	5.94
	7.07	4.97
	6.98	7.25

Table 4.1 shows the both aromatic and  $\text{CH}_2$  protons belonging to the benzyl moiety of the salts. As can be seen, both signals appear in 6.98-7.49 and 4.97-7.25 ppm region and varies depending on the heteroatoms and substituents.

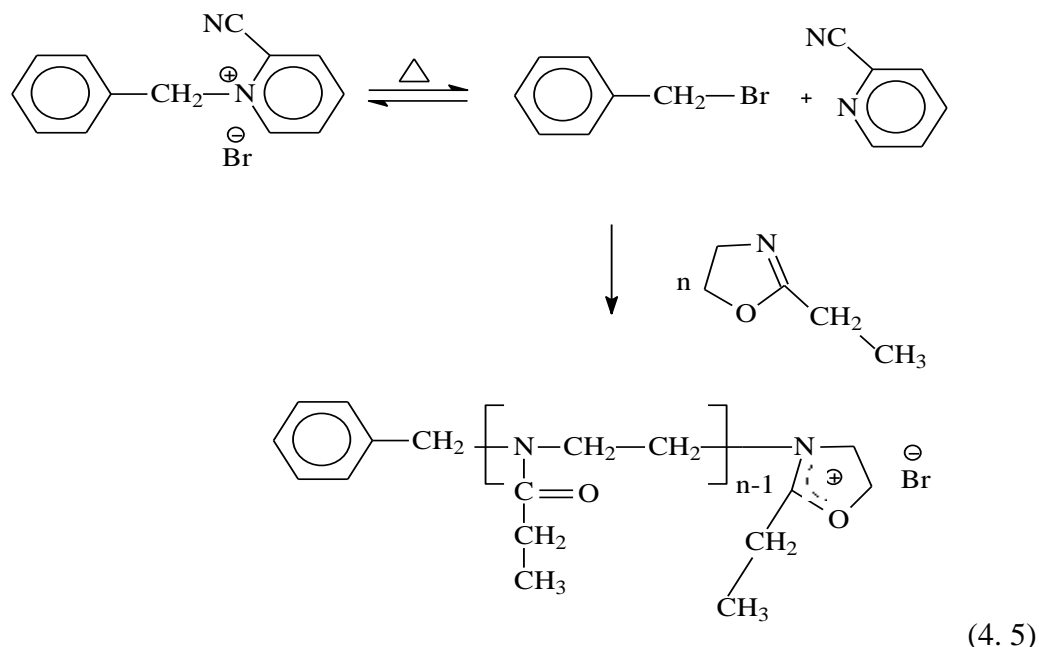
## 4.2 Externally Stimulated Cationic Polymerization of EOZO

In accordance with the initiating role of benzyl bromide, it was attempted to generate such species with an external stimulation such as thermal and photochemical treatments.

### 4.2.1 Thermally Induced Cationic Polymerization of EOZO

As indicated in the theoretical part benzyl pyridinium type salts generate benzylic cations upon thermolysis. In the case of bromide salts, benzyl bromide is expected to

be formed. The cationic polymerization of EOZO then proceeds in the usual manner. The general reactions concerning benzyl bromide formation and subsequent polymerization are given below for the case of *N*-Benzyl-*o*-cyanopyridinium bromide salt.



The results of thermal polymerization of EOZO using various salts are collected in Table 4.2.

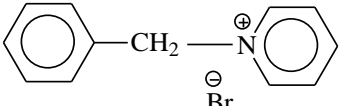
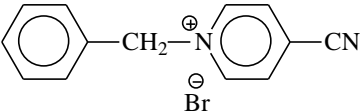
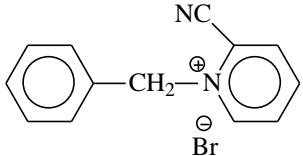
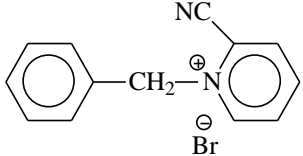
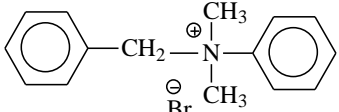
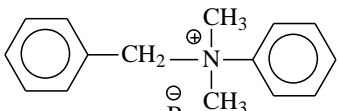
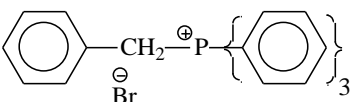
As can be seen, unsubstituted benzyl pyridinium salt is ineffective in initiation of the polymerization. Similarly *p*-CN derivative also does not induce the polymerization.

Electron withdrawing cyano group favours the  $\text{C-N}$  bond cleavage, hence the rate of benzyl cation generation is increased. Interestingly when CN group is in the *ortho* position the conversion to polymer is highest. This is probably related to the termination of polymerization by free pyridine groups formed in the thermolysis. This behavior was investigated by Endo and coworkers in detail [49]. According to Endo, the attack of pyridine groups at the early stages of the polymerization is only a minor process.

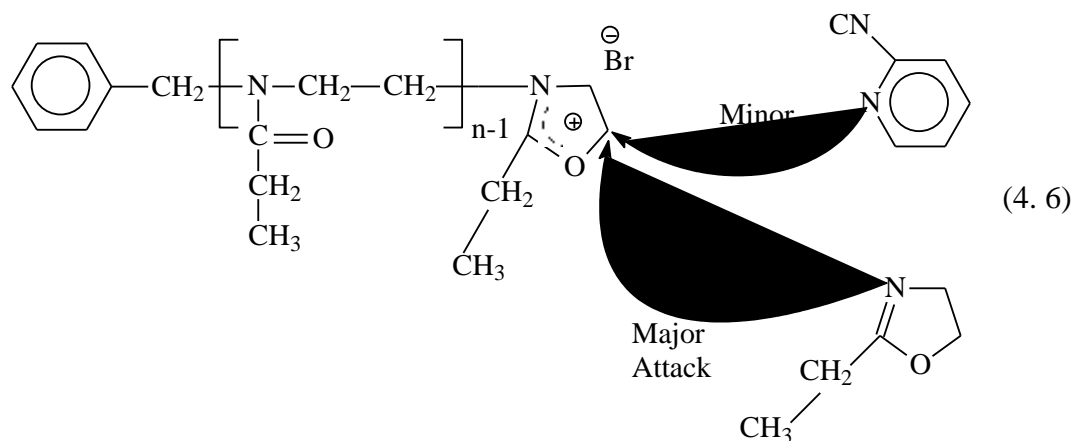
However when the concentration of pyridine increased it may become major attack and polymerization may be terminated. *N*-Benzyl pyridinium salts with various *p*-substituent in the pyridinium moiety was studied [49] in order to observe the

electrostatic effect. The polymerization activity of *N*-benzyl *p*-substituent pyridinium salt decreased in order to  $\text{CN} > \text{H} > \text{CH}_3 > \text{N}(\text{CH}_3)_2$ , indicating that the electron withdrawing group enhanced the leaving ability of the pyridine moiety from the salt. Benzyl *o*-CN pyridinium salt is 100 time more reactive than the corresponding *p*-CN derivatives. Thus, introduction of the *o*-cyano group into pyridine nucleo causes a large enhancement of the initiator activity. The reason for the activity enhancement by this modification can be accounted for by both electronic and steric effects of the *o*-cyano group of the pyridine group.

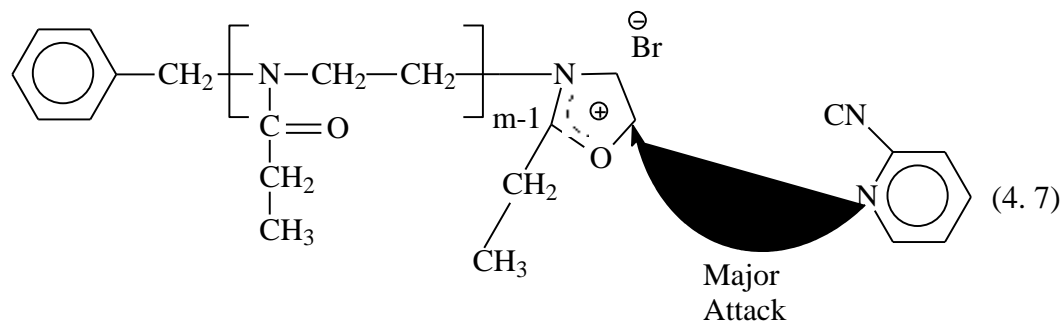
Table 4.2. Thermally Initiated Cationic Polymerization of 2-Ethyl-2-Oxazoline by Cationic Salts

Code	Initiator	Time (h)	Temp. (°C)	Conv. %	Mn	Mn/Mw
P 1		6	105	-	-	-
P 2		6	105	-	-	-
P 3a		6	105	70	3500	1.92
P 3b		24	105	71.5	3300	1.68
P 4a		6	105	55	1100	1.45
P 4b		18	105	99.9	3300	1.48
P 5a		6	105	-	-	-

Early stages of the polymerization: EOZO concentration is high and monomer addition is dominant process.



Late stages of the polymerization: EOZO concentration is low and the nucleophilic attack of pyridine becomes major process. ( $m > n$ )



In our work, the salt with o-cyano pyridine in which the nucleophilic attack is sterically lowered.

As can also be seen from the Table 4.2 polymerization yield and molecular weight of the resulting polymer do not change after 6 hour thermolysis.

It is also interesting to note the reactivity of *N,N*-dimethyl anilinium salts. These salts are known to generate benzylic cations in a similar way.





the polymers obtained by thermal initiation using *N*-Benzyl-*o*-cyanopyridinium bromide and *N*-Benzyl-*N,N*-dimethylanilinium bromide salts, respectively.

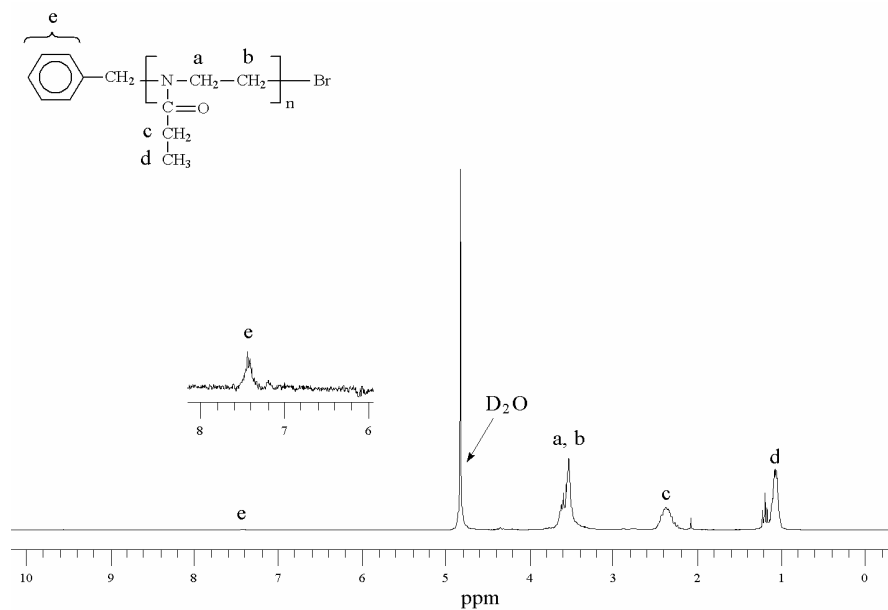


Figure 4.1.  $^1\text{H}$ -NMR Spectra of Poly EOZO initiated by *N*-Benzyl-*o*-cyanopyridinium Bromide (6 h.)

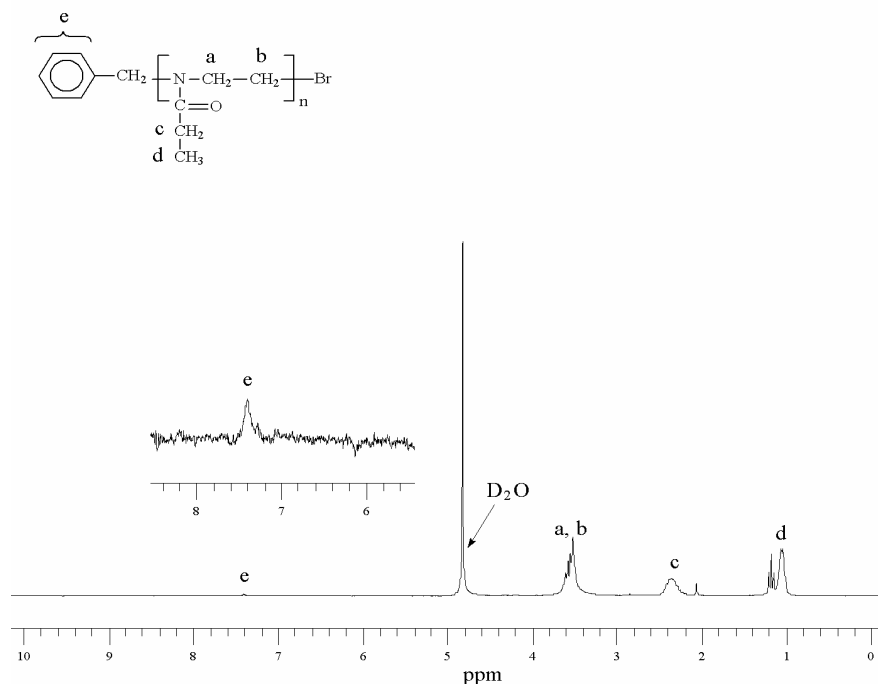


Figure 4.2.  $^1\text{H}$ -NMR Spectra of Poly EOZO initiated by *N*-Benzyl-*N,N*-dimethylanilinium Bromide (6 h.).

Both spectra represent characteristic signals of the polymer, i. e.  $-\text{CH}_3$  protons at 1.0-1.1 ppm,  $-\text{CO}-\text{CH}_2-$  protons at 2.2-2.4 ppm,  $-\text{CH}_2-\text{CH}_2-$  protons at 3.4-3.6 .

Moreover aromatic protons at benzylic group appear in 7.50 ppm region indicating incorporation of benzylic moiety and therefore, initiation by benzyl bromide.

We have also examined the  $^1\text{H}$ -NMR spectra of the polymerization mixture. In this case, polymerizations were performed in an NMR tube containing deuterio acetonitrile, monomer and the initiating salt. Figure 4.3 shows that  $^1\text{H}$ -NMR spectra before and after 6 hour polymerization time. The new peaks appearing in the range of 2.4-3.6 ppm corresponds to the propagating oxonium ions [56].

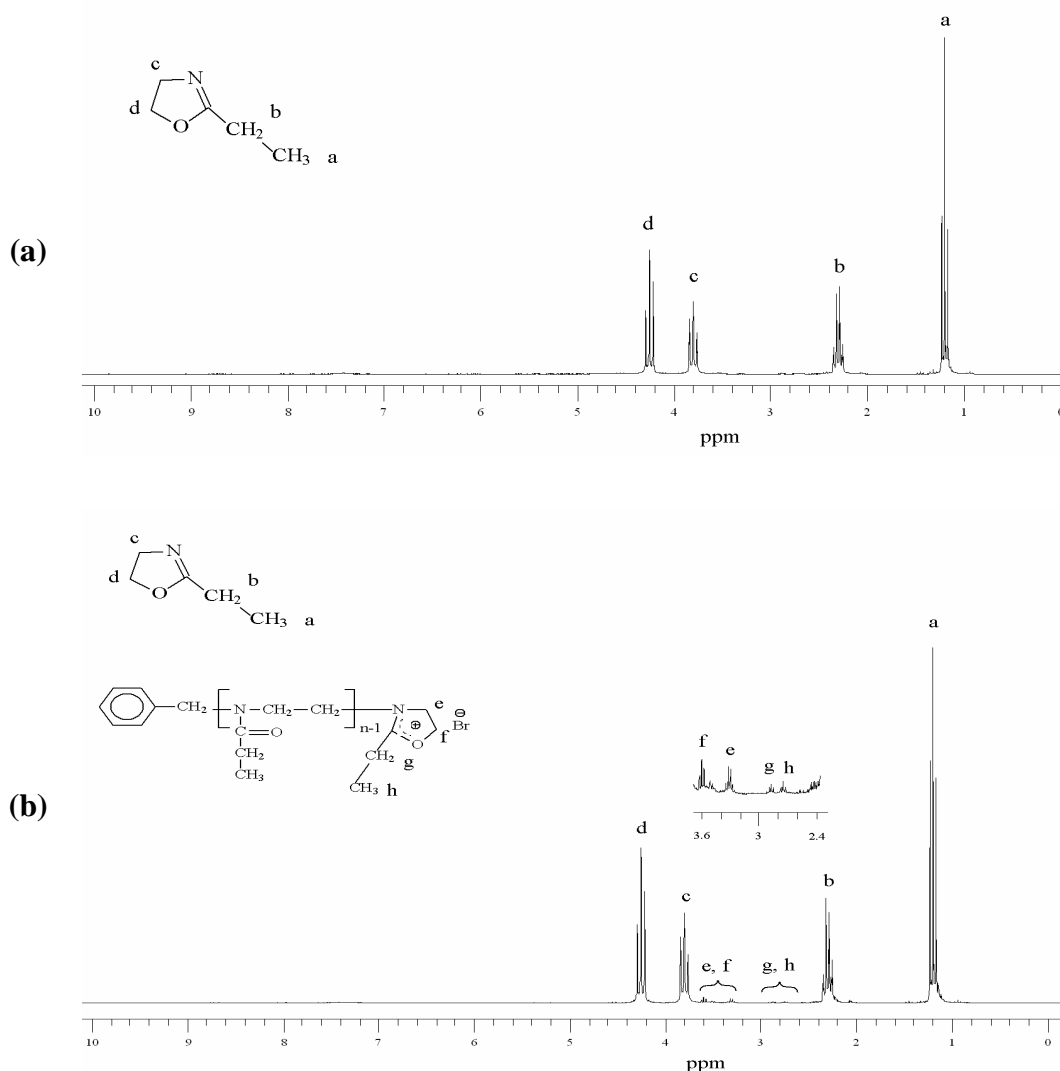
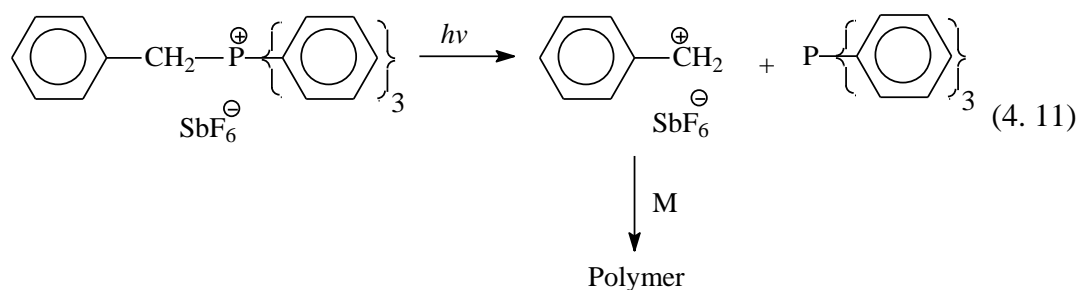
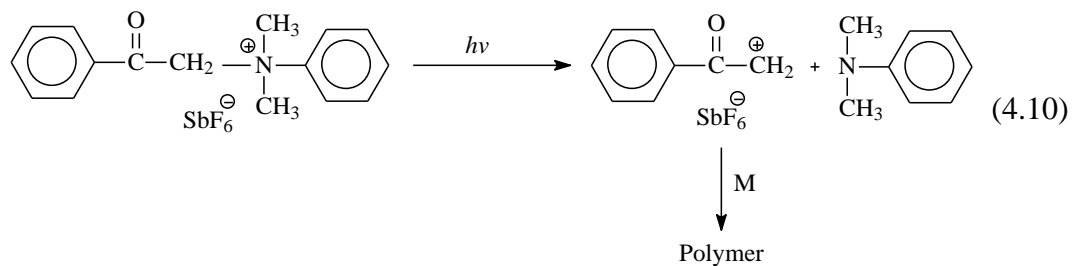


Figure 4.3.  $^1\text{H}$ -NMR Spectra of the Polymerization of EOZO Initiated by *N*-Benzyl-*o*-cyanopyridinium bromide in  $\text{CD}_3\text{CN}$  at  $105^\circ\text{C}$  (a): after 20 min. (b): after 6 hour.

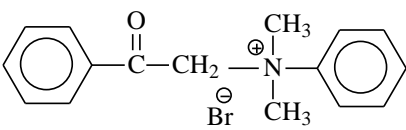
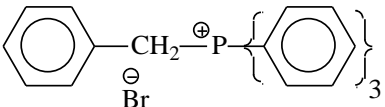
#### 4.2.2 Photochemically Induced Cationic Polymerization of EOZO

We have tested two photoactive salts in promoting cationic polymerization of EOZO. These salts with non-nucleophilic counter anion are known to decompose upon photolysis according to the following reactions.



Attempts to polymerization of EOZO with the above salts possessing bromide counter anions failed to produce polymers after 6 hour irradiation at room temperature and also at 65 °C (Table 4.3.)

Table 4.3. Photoinitiated Cationic Polymerization of 2-Ethyl-2-Oxazoline by Cationic Salts

Code	Initiator	Time	Temp.	Conv. %	Mn	Mn/Mw
P 4c		6	r.t.	-	-	-
P 5b		6	65	-	-	-

This behaviour may be due to the inefficiency of phenacyl bromide in initiating the polymerization of EOZO by itself. Indeed, in an independent experiment phenacylium bromide did not initiate the polymerization of EOZO after thermolysis at 65 °C for 6 hour.

In the case of phosphonium salt, photoinduced decomposition may be similar to thermally induced decomposition which is showed in (4. 9) and (4. 10), (4.11).

## 5. CONCLUSIONS

Cationic polymerization of 2-Ethyl-2-oxazoline can be achieved by using ammonium type salts. Among the various salts used, pyridinium salts were found to be the most efficient.

Electron withdrawing substituents on the pyridine moiety particularly at ortho position had a positive effect on the polymerization rate. Polymerization mechanism involves thermal dissociation of the salt which yields benzyl bromide. Photochemical dissociation was found to be inefficient.

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